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# X-RAY STUDIES OF COMPOUNDS IN THE SYSTEMS $\text{PbO-B}_2\text{O}_3$ AND $\text{K}_2\text{O-PbO-SiO}_2$

By Howard F. McMurdie

## ABSTRACT

X-ray diffraction data as determined from powder patterns of 10 compounds occurring in the systems  $\text{PbO-B}_2\text{O}_3$  and  $\text{K}_2\text{O-PbO-SiO}_2$  are published as a supplement to the phase equilibrium work previously reported on these systems. These data may be useful in related studies for identification of phases. The unit cell of  $\text{K}_2\text{O} \cdot 2\text{PbO} \cdot 2\text{SiO}_2$  was determined and a possible atomic arrangement outlined.

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## I. INTRODUCTION

Reports have been published on the systems  $\text{PbO-SiO}_2$  [1],  $\text{K}_2\text{O-PbO-SiO}_2$  [2],  $\text{PbO-B}_2\text{O}_3$  [3], and  $\text{PbO-B}_2\text{O}_3\text{-SiO}_2$  [4] by the National Bureau of Standards. These phase equilibrium studies are of interest to investigators of lead glazes, enamels, and glasses. X-ray diffraction patterns have been reported for compounds in the system  $\text{PbO-SiO}_2$  [5] and for the ternary compound,  $5\text{PbO} \cdot \text{B}_2\text{O}_3 \cdot \text{SiO}_2$  [4]. Since X-ray powder patterns of crystalline phases aid in most investigations of these or related systems, it has been thought desirable to publish X-ray data for compounds in the systems  $\text{PbO-B}_2\text{O}_3$  and  $\text{K}_2\text{O-PbO-SiO}_2$ . This present report completes the data pertaining to the patterns of all of the stable lead compounds so far mentioned in these four systems.

## II. METHODS

The methods used in the preparation of the compounds and their identification by means of the polarizing microscope, together with the optical properties as measured by the microscope, have been given in the reports mentioned.

For the preparation of the powder patterns, the powdered samples were mounted on fine glass rods in the center of cylindrical cameras, having radii of about 5.7 cm, and were rotated during exposure.  $\text{CuK}_\alpha$  radiation was used. The radii of the cameras were checked by

<sup>1</sup> Figures in brackets indicate the literature references at the end of this paper.

NaCl. The positions of the lines on the film were measured to 0.1 mm and the relative intensities were calculated.

### III. RESULTS

In most cases the compounds are of such low symmetry that it is very difficult, if not impossible, to index the lines. However, one of the compounds ( $\text{K}_2\text{O} \cdot 2\text{PbO} \cdot 2\text{SiO}_2$ ) is hexagonal and its unit cell has been measured.

Tables 1 to 6 give the interplanar spacings and estimated relative intensities for the following lead borates:  $\alpha 4\text{PbO} \cdot \text{B}_2\text{O}_3$ ,  $\beta 4\text{PbO} \cdot \text{B}_2\text{O}_3$ ,  $\alpha 2\text{PbO} \cdot \text{B}_2\text{O}_3$ ,  $\beta 2\text{PbO} \cdot \text{B}_2\text{O}_3$ ,  $5\text{PbO} \cdot 4\text{B}_2\text{O}_3$ , and  $\text{PbO} \cdot 2\text{B}_2\text{O}_3$ .

Tables 7 to 9 give similar data for three of the ternary compounds ( $\text{K}_2\text{O} \cdot 4\text{PbO} \cdot 8\text{SiO}_2$ ,  $\text{K}_2\text{O} \cdot \text{PbO} \cdot 4\text{SiO}_2$ , and  $\text{K}_2\text{O} \cdot 2\text{PbO} \cdot 2\text{SiO}_2$ ) occurring in the system  $\text{K}_2\text{O}$ - $\text{PbO}$ - $\text{SiO}_2$ . Because of the instability of  $2\text{K}_2\text{O} \cdot \text{PbO} \cdot 3\text{SiO}_2$ , an X-ray pattern was not made. The compound in table 10 designated as "unknown" is identical with that referred to in the original work on the system as a "fifth compound." Its composition has not been determined.

$\text{K}_2\text{O} \cdot 2\text{PbO} \cdot 2\text{SiO}_2$  crystallizes in hexagonal plates and is optically uniaxial. The pattern, represented by data given in table 9, was found to fit a hexagonal lattice with  $a = 5.62 \pm 0.02$  Å and  $c = 7.57 \pm 0.02$  Å. The spacings calculated for the various planes using these values are given in the last column. With one molecule to the unit cell, this size gives a calculated density of 5.25. The density determined by pycnometer was 5.15. Considering that the sample contained some glass, this is good agreement.

Study of the reflections present shows no regular halving; thus several space groups are possible. Intensity calculations on a few simple planes indicate that very probably the atoms are arranged as follows in  $\text{C}_{3i}$ :

2 K in 2 d	$(1/3 \ 2/3 \ z)$	$(2/3 \ 1/3 \ \bar{z})$	[6]	$z \approx 0.5$
2 Pb in 2 d	$(1/3 \ 2/3 \ z)$	$(2/3 \ 1/3 \ \bar{z})$		$z \approx 0$
2 Si in 2 c	$(0 \ 0 \ z)$	$(0 \ 0 \ \bar{z})$		$z \approx .28$
1 O in 1 b	$(0 \ 0 \ 1/2)$			
6 O in 6 g	$(x \ y \ z)$	etc.		$z \approx .18$

Such an arrangement gives a structure consisting of two silica tetrahedrons with a single shared oxygen (at  $0 \ 0 \ 1/2$ ). The K and Pb atoms are each equidistant from six oxygen atoms. The  $x$  and  $y$  parameters for the oxygen atoms were not determined. If they have a simple ratio, it might result in the crystal having the symmetry of a higher space group, such as  $\text{D}_{3d}^1$  or  $\text{D}_{3d}^2$ .

### IV. SUMMARY

The X-ray diffraction patterns for 10 compounds occurring in the systems  $\text{PbO}$ - $\text{B}_2\text{O}_3$  and  $\text{K}_2\text{O}$ - $\text{PbO}$ - $\text{SiO}_2$  have been determined. These can be used by workers in related studies for identification of crystal-line phases. The unit cell of  $\text{K}_2\text{O} \cdot 2\text{PbO} \cdot 2\text{SiO}_2$  was determined and a tentative structure outlined.

The author is grateful to E. N. Bunting for the preparation and identification of the specimens examined and for the determination of the density of  $\text{K}_2\text{O} \cdot 2\text{PbO} \cdot 2\text{SiO}_2$ .

## V. REFERENCES

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 [4] R. F. Geller and E. N. Bunting, *The system PbO-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>*, J. Research NBS **23**, 275 (1939) RP1231.  
 [5] H. F. McMurdie and E. N. Bunting, *X-ray studies of compounds in the system PbO-SiO<sub>2</sub>*, J. Research NBS **23**, 543 (1939) RP1251.  
 [6] R. W. G. Wyckoff, Analytical expression of the results of the theory of space groups. Carnegie Institution of Washington (1930).

TABLE 1.—Interplanar spacing of  $\alpha\text{PbO.B}_2\text{O}_3$ 

[VS=very strong; VW=very weak; M=medium; S=strong; W=weak]

Estimated intensity	d	Estimated intensity	d
	<i>A</i>		<i>A</i>
W.....	4.20	M.....	2.280
W.....	3.87	W.....	2.248
S.....	3.59	W.....	2.093
M.....	3.44	VW.....	2.070
M.....	3.34	VW.....	1.916
VS.....	3.12	VW.....	1.893
M.....	3.07	VW.....	1.854
M.....	3.00	S.....	1.799
W.....	2.94	M.....	1.769
S.....	2.86	VW.....	1.754
W.....	2.71	VW.....	1.735
VW.....	2.55	S.....	1.708
VW.....	2.435	M.....	1.659
W.....	2.379	S.....	1.646

TABLE 2.—Interplanar spacing of  $\beta 4\text{PbO.B}_2\text{O}_3$ 

[VS=very strong; VW=very weak; M=medium; S=strong; W=weak]

Estimated intensity	d	Estimated intensity	d
	<i>A</i>		<i>A</i>
M.....	4.58	VW.....	2.075
W.....	3.92	M.....	1.955
W.....	3.79	M.....	1.890
VW.....	3.26	VW.....	1.868
VS.....	3.07	W.....	1.836
S.....	3.02	M.....	1.802
VW.....	2.94	VW.....	1.776
S.....	2.87	VW.....	1.750
M.....	2.75	VW.....	1.738
W.....	2.69	W.....	1.699
VW.....	2.63	VW.....	1.654
M.....	2.49	VW.....	1.632
VW.....	2.320	W.....	1.616
W.....	2.258	W.....	1.590
W.....	2.200	VW.....	1.558
VW.....	2.160	W.....	1.542

TABLE 3.—*Interplanar spacing of  $\alpha 2\text{PbO} \cdot \text{B}_2\text{O}_3$* 

[VS=very strong; VW=very weak; M=medium; S=strong; W=weak]

Estimated intensity	<i>d</i>	Estimated intensity	<i>d</i>
	<i>A</i>		<i>A</i>
VW.....	7.2	VW.....	2.56
M.....	5.81	S.....	2.40
VW.....	5.52	M.....	2.25
VW.....	3.90	W.....	2.09
VS.....	3.62	M.....	2.043
VS.....	3.39	M.....	1.984
M.....	3.26	S.....	1.951
VS.....	3.18	W.....	1.879
W.....	2.97	M.....	1.826
M.....	2.88	W.....	1.808
W.....	2.76	M.....	1.720
W.....	2.70	M.....	1.702
M.....	2.60	W.....	1.670

TABLE 4.—*Interplanar spacing of  $\beta 2\text{PbO} \cdot \text{B}_2\text{O}_3$* 

[VS=very strong; VW=very weak; M=medium; S=strong; W=weak]

Estimated intensity	<i>d</i>	Estimated intensity	<i>d</i>
	<i>A</i>		<i>A</i>
W.....	6.54	M.....	2.292
S.....	5.55	VW.....	2.242
VW.....	4.66	VW.....	2.200
M.....	3.67	W.....	2.155
M.....	3.52	S.....	2.034
S.....	3.42	VW.....	1.984
VS.....	3.05	M.....	1.943
S.....	3.00	VW.....	1.912
M.....	2.92	VW.....	1.894
M.....	2.82	W.....	1.868
M.....	2.78	W.....	1.826
M.....	2.74	W.....	1.805
W.....	2.56	W.....	1.760
W.....	2.53	W.....	1.741
W.....	2.49	W.....	1.714
VW.....	2.366	W.....	1.690

TABLE 5.—*Interplanar spacing of  $5\text{PbO} \cdot 4\text{B}_2\text{O}_3$* 

[VS=very strong; VW=very weak; M=medium; S=strong; W=weak]

Estimated intensity	<i>d</i>	Estimated intensity	<i>d</i>
	<i>A</i>		<i>A</i>
VS.....	5.89	VW.....	1.905
M.....	4.86	VW.....	1.840
W.....	4.45	VW.....	1.809
S.....	3.70	VW.....	1.779
VS.....	3.39	M.....	1.738
VS.....	3.16	VW.....	1.696
VS.....	3.07	M.....	1.662
M.....	2.96	W.....	1.643
VW.....	2.83	M.....	1.591
W.....	2.71	W.....	1.549
W.....	2.60	W.....	1.519
VW.....	2.280	W.....	1.486
VS.....	2.185	M.....	1.451
S.....	2.070	VW.....	1.425
M.....	2.009	VW.....	1.395
S.....	1.936	W.....	1.371

TABLE 6.—*Interplanar spacing of PbO.2B<sub>2</sub>O<sub>3</sub>*

[VS=very strong; VW=very weak; M=medium; S=strong; W=weak]

Estimated intensity	<i>d</i>	Estimated intensity	<i>d</i>
	<i>A</i>		<i>A</i>
S.....	5.46	S.....	1.890
S.....	4.12	W.....	1.854
S.....	3.96	M.....	1.805
S.....	3.07	M.....	1.729
M.....	2.96	M.....	1.690
S.....	2.80	W.....	1.667
S.....	2.75	VW.....	1.593
VS.....	2.68	S.....	1.556
W.....	2.314	W.....	1.535
W.....	2.231	W.....	1.521
VW.....	2.185	W.....	1.482
W.....	2.116	M.....	1.457
W.....	2.052	M.....	1.437
VS.....	2.025	W.....	1.406
M.....	1.975	W.....	1.393
S.....	1.939	W.....	1.375

TABLE 7.—*Interplanar spacing of K<sub>2</sub>O.4PbO.8SiO<sub>2</sub>*

[VS=very strong; VW=very weak; M=medium; S=strong; W=weak]

Estimated intensity	<i>d</i>	Estimated intensity	<i>d</i>
	<i>A</i>		<i>A</i>
VS.....	8.32	W.....	2.079
M.....	6.59	W.....	2.061
M.....	5.89	W.....	2.009
VW.....	4.38	W.....	1.963
VW.....	4.20	VW.....	1.936
VW.....	3.96	W.....	1.795
W.....	3.73	M.....	1.760
VS.....	3.52	M.....	1.717
S.....	3.29	W.....	1.687
S.....	2.78	VW.....	1.670
S.....	2.71	W.....	1.614
VW.....	2.63	W.....	1.583
W.....	2.58	W.....	1.564
M.....	2.367	M.....	1.512
W.....	2.308	M.....	1.467
VW.....	2.263	M.....	1.439

TABLE 8.—*Interplanar spacing of K<sub>2</sub>O.PbO.4SiO<sub>2</sub>*

[VS=very strong; VW=very weak; M=medium; S=strong; W=weak]

Estimated intensity	<i>d</i>	Estimated intensity	<i>d</i>
	<i>A</i>		<i>A</i>
S.....	6.22	VW.....	2.53
M.....	5.81	M.....	2.42
S.....	5.55	M.....	2.40
VW.....	5.20	VW.....	2.285
M.....	4.81	W.....	2.237
W.....	4.45	M.....	2.155
VS.....	3.70	VW.....	2.121
VW.....	3.50	VW.....	2.083
VW.....	3.33	VW.....	2.052
VS.....	3.22	W.....	2.021
VS.....	3.08	VW.....	1.959
S.....	2.99	VW.....	1.939
W.....	2.81	VW.....	1.912
W.....	2.76	VW.....	1.864
M.....	2.67	W.....	1.833
M.....	2.58		

TABLE 9.—*Interplanar spacing for  $K_2O \cdot 2PbO \cdot 2SiO_2$* [Based on  $a=5.62$  Å;  $c=7.57$  Å hexagonal lattice]

[VS=very strong; VW=very weak; M=medium; S=strong; W=weak]

Estimated intensity	$d$	$hkl$	$d$ (calculated)
S.....	7.5	001	7.6
W.....	4.83	100	4.85
S.....	4.08	101	4.08
VS.....	2.98	102	2.98
S.....	2.80	110	2.80
M.....	2.62	111	2.63
VW.....	2.52	003	2.52
W.....	2.42	200	2.43
VW.....	2.314	201	2.32
M.....	2.237	103-112	2.242
S.....	2.043	202	2.040
M.....	1.893	004	1.893
VW.....	1.833	120	1.840
W.....	1.779	121	1.782
M.....	1.760	104	1.765
S.....	1.656	122	1.655
M.....	1.619	300	1.619
VW.....	1.578	301	1.582
W.....	1.568	114	1.568
VW.....	1.516	005	1.514

TABLE 10.—*Interplanar spacing of  $K_2O \cdot PbO \cdot SiO_2$  compound of unknown composition*<sup>a</sup>

[VS=very strong; VW=very weak; M=medium; S=strong; W=weak]

Estimated intensity	$d$	Estimated intensity	$d$
S.....	8.32	VW.....	2.42
W.....	6.05	M.....	2.30
W.....	5.85	VW.....	2.23
VW.....	4.36	VW.....	2.165
VW.....	4.12	M.....	2.070
VS.....	3.51	W.....	1.996
W.....	3.18	M.....	1.939
W.....	2.95	W.....	1.833
M.....	2.84	M.....	1.729
M.....	2.74	S.....	1.703
M.....	2.65	W.....	1.618
W.....	2.51		

<sup>a</sup> This compound was reported as a primary phase in a small field adjacent to the silica field. It melts incongruently.

WASHINGTON, March 22, 1941.